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Problems with Newman's Numerical Technique -
A Comparison with deBoor's Solver

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by

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Introduction

Newman's numerical technique (1-4) has been used extensively to solve two-point boundary value problems consisting of coupled, ordinary differential equations. Unfortunately, his method does not always yield a solution to a system of independent equations. Sometimes his algorithm (BAND) signals incorrectly that the coefficient matrix is singular (e.g., DETERMINANT=0 AT J=2). In addition, no solution is obtained to the system of equations. This problem is referred to as the "zero determinant problem" throughout the rest of this note. The cause of the problem, which has not been identified, seems to be numerical and related to the way in which the BAND algorithm manipulates the system of matrix equations. Fortunately, an algorithm by deBoor (5) has been successful in some cases where BAND fails.

Example System

While debugging a computer program for a model of the lithium/thionyl chloride cell, the authors suspected that the BAND algorithm was not working correctly because of the zero determinant problem. Initially, six equations and six unknowns were used to describe the system shown in Fig. 1 in one spatial dimension (x). Later, this system was reduced to two equations and two unknowns. Even this reduced system exhibited the zero determinant problem.

The six equation set and the two equation set are referred to as the "full set" and the "reduced set," respectively. The full set of equations for the region and boundaries shown in Fig. 1 are given in Table I. A description of the equations and unknowns in Table I is beyond the scope of this note. Table II is a listing of the values used for the constants appearing in these equations. The unknowns v^{\square} , ϵ ,

i_2 , and Φ_1 and Eq. [2] - [5], [8] - [11], and [14] - [17] can be eliminated from the full set because these equations are not coupled with the remaining equations. The reduced set consists of two equations and two unknowns (c and Φ_2) as shown in Table III. The initial condition for c , for both the full set and the reduced set, is $c(0, x) = c_{init}$.

Solution Methods

The ordinary and partial differential equations listed above were written in finite difference form and programmed for solution using the procedure for Newman's BAND algorithm (2, 3). Implicit stepping (6) was used for the time derivatives. To use deBoor's solver, instead of BAND, several subprograms were written to make the transition simple. These subprograms along with the examples given here are available from the authors.

Newman's algorithm and deBoor's solver were written specifically to solve systems having banded coefficient matrices. A full-matrix solver called LEQTIF (7) was used to provide a basis for comparison between the these two banded system solvers.

Observations

The zero determinant problem of Newman's BAND algorithm is very sensitive to the finite difference expression used for the gradient of Φ_2 in Eq. [12] and to the location of the origin of the coordinate system. The gradient of Φ_2 , $\partial\Phi_2/\partial x$, can be approximated with central, forward, or backward finite difference expressions as

follows:

Central difference (CD)

$$\frac{\partial \Phi_2}{\partial x} = \frac{\Phi_2(j+1) - \Phi_2(j-1)}{2h} \quad [19]$$

Forward difference (FD)

$$\frac{\partial \Phi_2}{\partial x} = \frac{\Phi_2(j+1) - \Phi_2(j)}{h} \quad [20]$$

Backward difference (BD)

$$\frac{\partial \Phi_2}{\partial x} = \frac{\Phi_2(j) - \Phi_2(j-1)}{h} \quad [21]$$

These difference expressions are accurate to order h^2 , h , and h , respectively. Three point forward and backward differences, accurate to h^2 , were used for derivative boundary conditions such as Eq. [2]. A ten node grid is shown in Fig. 1 where the numbering of the nodes depends on the origin of the coordinate system. The system of equations can be solved by first evaluating the set of equations at $x = a$ and proceeding to $x = b$ (coordinate system #1, CS1) or by starting at $x = b$ and proceeding to $x = a$ (coordinate system #2, CS2). Several attempts were made to solve the example system using combinations of the following: the full set or the reduced set of equations; one of the difference formulas, CD, FD, or BD; one of the two coordinate systems, CS1 or CS2; and Newman's algorithm or deBoor's solver. A run was designated successful when the solution shown in Fig. 2 was obtained, a failure when the solver indicated that the numerical system was singular (i.e., a zero determinant was indicated), and nonconvergent if convergence was not achieved.

Table IV shows that deBoor's solver works in some instances where Newman's technique does not, but never the other way around. Note that for both sets of

equations for CS1 deBoor's solver fails for the FD case, whereas for CS2 deBoor's solver fails for the BD case. Thus the failure of deBoor's solver is at least consistent with the coordinate system. On the other hand, the results of Newman's technique are different when using either the full set or the reduced set, even in cases which are otherwise identical.

Two items that were thought to be responsible for the zero determinant problem were the initial guesses of the unknowns and the precision used for the variables in the computer program. To test the first of these, the initial guesses were set equal to the values obtained from the successful CD cases. This change had a slight effect on the results in Table IV; three cases were changed from failures to nonconvergent cases. The precision of the variables was checked by using different computers: a HP-9000 (series 500) and a VAX 8800. Double precision was used on the HP and quadruple precision on the VAX. The same results were obtained from both computers.

A few other variations on some of the cases in Table IV were tried to determine if these results were obtained consistently. The number of nodes was increased from 10 to 100, thus decreasing h by an order of magnitude, and the time step was decreased from 1×10^{-3} seconds to 1×10^{-6} seconds. These changes had no effect on the cases studied. Next, the ordering of the equations in the full set was changed. Although this change had no effect on the failure or success of a run, it was observed that Newman's technique behaved in a slightly different manner. That is, the determinant was flagged as zero at different nodes. For example, for CS1 and CD, the determinant was signalled as zero at node 2 for one particular ordering of the equations describing the reservoir (Eq. [7], [12], [9], [10], [11], and [8]). When the equations were reordered (Eq. [7], [8], [9], [10], [11], and [12]) the determinant was signalled as zero at both nodes 2 and 10.

Although deBoor's solver fails fewer times than does Newman's technique, deBoor's method still fails in some cases. To determine if these failures were due to limitations within deBoor's method a full-matrix solver, LEQTIF from the IMSL library (7), was used to solve the reduced set. LEQTIF and deBoor's method exhibited the same performance as shown in Table IV.

As far as CPU time is concerned, little difference exists between the two methods. For six unknowns and 100 nodes deBoor's solver requires 22.72 seconds of CPU time and Newman's technique requires 23.91 seconds on the VAX 8800. However, the storage requirements are much greater for deBoor's algorithm than for Newman's algorithm. When many unknowns and nodes are involved, the large amount of memory required by deBoor's algorithm may become prohibitive especially for microcomputers.

Conclusion

Newman's numerical technique does not yield a solution to a given set of equations in some instances. For some of these cases in which Newman's technique does not work a solver by deBoor (5) does work and therefore it seems to be a more robust algorithm. Consequently, it is recommended that deBoor's solver be used during program development; later, one may wish to switch to Newman's technique to save memory, especially if a large number of unknowns and node points are involved.

List of Symbols

c	concentration of electrolyte, mol/cm^3
c_{init}	initial concentration of electrolyte, mol/cm^3
c_o	concentration of the solvent, mol/cm^3
c_{ref}	reference concentration of electrolyte, mol/cm^3
D	diffusion coefficient of the binary electrolyte, cm^2/s
F	Faraday's constant, $96487 \text{ C}/\text{mol of electrons}$
h	distance between successive nodes, cm
$i_{o,we,ref}$	exchange current density of working electrode reaction at c_{ref} , A/cm^2
i_2	superficial current density in the solution phase, A/cm^2
I	total cell current density (applied), A/cm^2
j	j^{th} node
n	number of electrons transferred in the electrode reaction
R	universal gas constant, $8.3143 \text{ J}/\text{mol} \cdot \text{K}$
s_i	stoichiometric coefficient of species i
T	absolute temperature, K
t	time, s
t_i^\square	transference number of species i relative to \mathbf{v}^\square
U_{ref}	Potential of the electrode electrochemical reaction relative to the reference electrode, V
\tilde{V}_e	partial molar volume of electrolyte, cm^3/mol
\tilde{V}_o	partial molar volume of solvent, cm^3/mol
\mathbf{v}^\square	superficial volume average velocity, cm/s
x	radial dimension, cm
z_i	charge number of species i

Greek Symbols

α_a	transfer coefficient in the anodic direction
α_c	transfer coefficient in the cathodic direction
γ	exponent for the concentration ratio in the Butler-Volmer equation
ϵ	porosity or void volume fraction
κ	conductivity of the solution, $\Omega^{-1}\text{cm}^{-1}$
ν	number of cations and anions produced by dissociation of electrolyte
ν_+	number of cations produced by dissociation of electrolyte
Φ_1	potential in the matrix phase, V
Φ_2	potential in the electrolyte, V

List of Symbols (Continued)

Subscripts

o	solvent
we	working electrode
$+$	cation
1	solid matrix phase
2	electrolyte phase

References

1. J. Newman, *Ind. Eng. Chem. Fundam.*, **7**, 514 (1968).
2. J. S. Newman, "Electrochemical System." Prentice Hall, Inc., Englewood Cliffs, NJ (1971).
3. R. E. White, *Ind. Eng. Chem. Fundam.*, **17**, 367 (1978).
4. J. Van Zee, G. Kleine, R. E. White, and J. Newman, in "Electrochemical Cell Design," R. E. White, Editor, p. 377, Plenum Publishing Co., New York (1984).
5. C. deBoor, "A Practical Guide to Splines," Springer-Verlag New York Inc., New York, NY (1978).
6. B. Carnahan, H. A. Luther, and J. O. Wilkes, "Applied Numerical Methods," John Wiley & Sons, New York, NY (1969).
7. IMSL, "User's Manual," International Mathematical and Statistical Libraries, Inc., Edition 9.2, Vol. 2 (1984).

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Table I. Full Set

Surface of reference electrode:

$$c = c_{init} \quad [1]$$

$$\nabla \cdot \mathbf{v}^\blacksquare = 0 \quad [2]$$

$$\epsilon = 1 \quad [3]$$

$$\Phi_1 = 0 \quad [4]$$

$$\mathbf{i}_2 = I \quad [5]$$

$$\Phi_2 = U_{ref} \quad [6]$$

Reservoir:

$$\frac{\partial c}{\partial t} = D\nabla^2 c - \nabla \cdot (c\mathbf{v}^\blacksquare) \quad [7]$$

$$\nabla \cdot \mathbf{v}^\blacksquare = 0 \quad [8]$$

$$\epsilon = 1 \quad [9]$$

$$\Phi_1 = 0 \quad [10]$$

$$\mathbf{i}_2 = I \quad [11]$$

$$\frac{I}{\kappa} = -\nabla\Phi_2 - \frac{\nu RT}{\mathbf{F}} \left(\frac{s_+}{n\nu_+} + \frac{t_+^\blacksquare}{z_+\nu_+} - \frac{s_o c \tilde{V}_o}{n(1 - c\tilde{V}_e)} \right) \frac{\nabla c}{c} \quad [12]$$

Surface of working electrode:

$$-D\nabla c + \frac{t_+^\blacksquare I}{z_+\nu_+ \mathbf{F}} = -\frac{s_+}{n\nu_+ \mathbf{F}} I \quad [13]$$

$$\mathbf{v}^\blacksquare = 0 \quad [14]$$

$$\epsilon = 1 \quad [15]$$

$$\mathbf{i}_2 = I \quad [16]$$

$$I = -i_{o,we,ref} \left(\frac{c}{c_{ref}} \right)^\gamma \left[\exp \left(\frac{\alpha_a \mathbf{F}}{\mathbf{RT}} (\Phi_1 - \Phi_2 - U_{ref,we}) \right) - \exp \left(-\frac{\alpha_c \mathbf{F}}{\mathbf{RT}} (\Phi_1 - \Phi_2 - U_{ref,we}) \right) \right] \quad [17]$$

Eq. [12]

Table II. Parameter values used to solve the example system

PARAMETER	VALUE
Gap between electrodes	0.01 cm
Number of node points	10
Time step	0.0001 s
Applied current density, I	0.08 A/cm ²
Diffusion coefficient, D	3.35×10^{-5} cm ² /s
Electrolyte conductivity, κ	0.0146 ohm ⁻¹ cm ⁻¹
Partial molar volume of electrolyte, \tilde{V}_e	77.97 cm ³ /mol
Partial molar volume of solvent, \tilde{V}_o	72.63 cm ³ /mol
Transference number of + species, t_+^\pm	0.5
Dissociation constant of + species, ν_+	1.0
Stoichiometric coefficient of + species, s_+	-2.0
Stoichiometric coefficient of solvent, s_o	-1.0
Number of electrons transferred, n	2
Exchange current density, $i_{o,we,ref}$	0.001 A/cm ²
Anodic transfer coefficient, α_a	1.0
Cathodic transfer coefficient, α_c	1.0
Working electrode reference potential, $U_{ref,we}$	0.0 V
Concentration exponent in Butler-Volmer Eq., γ	1.0
Reference electrolyte concentration, c_{ref}	0.001 mol/cm ³
Initial electrolyte concentration, c_{init}	0.001 mol/cm ³

Table III. Reduced Set

Surface of reference electrode:

Eq. [1]

Eq. [6]

Reservoir:

$$\frac{\partial c}{\partial t} = D \nabla^2 c \quad [18]$$

Eq. [12]

Surface of working electrode:

Eq. [13]

Eq. [12]

Table IV. Comparison of Newman's algorithm and deBoor's solver when applied to the example system

(NC - nonconvergent, F - failure, R - successful run)

Method	Coordinate System	—Full Set—			—Reduced Set—		
		BD	CD	FD	BD	CD	FD
Newman's BAND	# 1	R	F	F	R	F	F*
	# 2	F	F	F	NC	R	R
deBoor's solver	# 1	R	R	F	R	R	F*
	# 2	F	R	R	F*	R	R
LEQTIF (IMSL)	# 1				R	R	F*
	# 2				F	R	R

* These became NC when using the solution as the initial guess.

List of Figure Captions

- Fig. 1 Schematic representation of the example system –
two electrodes separated by an electrolyte.
- Fig. 2 Example system solution – electrolyte concentration
and solution potential profiles.

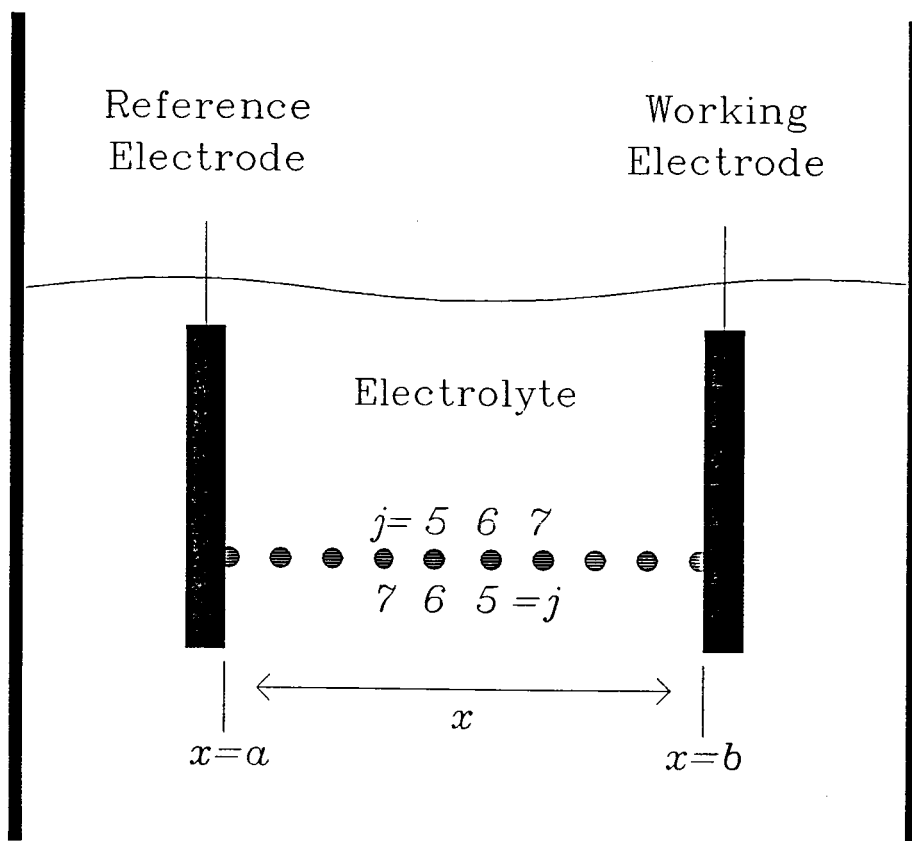


Figure 1. Evans and White

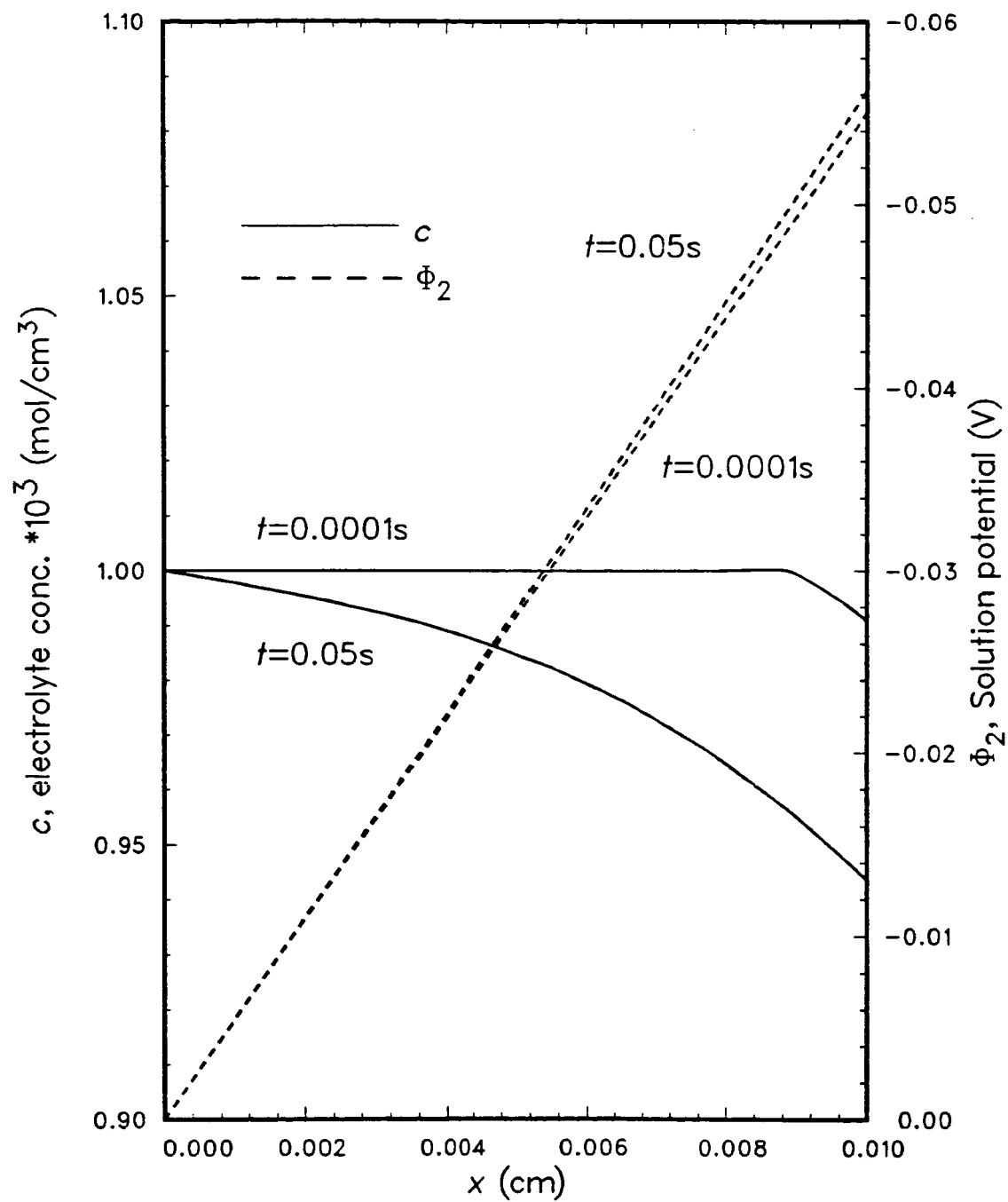


Figure 2. Evans and White